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Low-Temperature Oxidation of H₂/CH₄/C₂H₆/Ethanol/DME: Experiments and Modelling at High Pressures

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1. Objectives of the study

The main aim of this work was to measure the oxidation characteristics of H₂, CH₄, C₂H₆, DME, and ethanol at high pressures (20–100 bar) and low to intermediate temperatures (450–900 K) in a laminar flow reactor. Furthermore, a detailed chemical kinetic model was sought to address the oxidation of aforementioned fuels at high pressures.

2. Results

Figure 1 shows the results of the oxidation experiments in the laminar flow reactor for a stoichiometric mixture of H₂/O₂/N₂. Hydrogen oxidation started between 750 and 825 K for a wide range of stoichiometries ($\Phi = 0.001$ –12). The collected data were interpreted in terms of a detailed chemical kinetic model (for details see [1]) which was able to reproduce the measurements well.

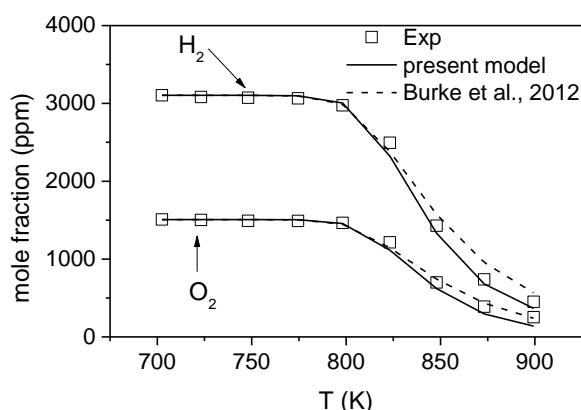


Figure 1. Results of stoichiometric experiments on hydrogen (0.31% H₂ and 0.15% O₂ in N₂, $\Phi = 1.03$) at 50 bar pressure.

Figure 2 represents the results of methane oxidation as well as the effect of doping the mixture with DME. For neat methane, the fuel conversion was detected above 750 K while replacing ~2% of methane by DME shifted the onset of fuel conversion to 725 K. Increasing the DME ratio to 3.2% triggered ignition at 700 K. The model for hydrocarbon oxidation is based on previous work from our laboratory (e.g. see [2]). The submodel for DME was based on a study by Zhao et al. [3] but several reactions were modified according to new determinations. As shown in Fig. 2, the predictions of the present model agreed well with the measured concentrations of major components. However, the DME was consumed at temperatures lower than those revealed by the experiments. The results of kinetic modelling indicated that high-pressure oxidation is highly affected by CH₃OO chemistry at T < 800 K.

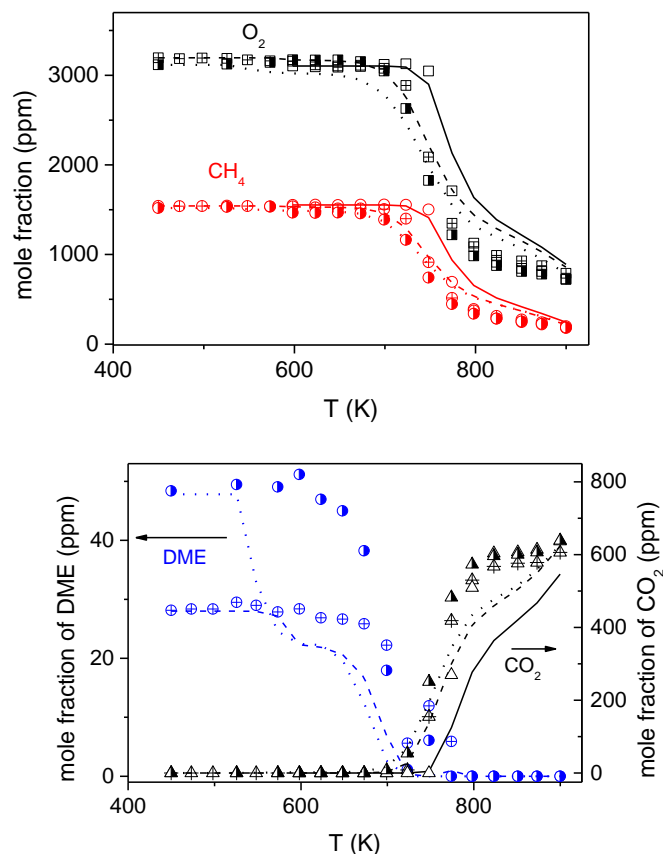


Figure 2. Results of stoichiometric experiments on neat methane (0.15% CH_4 and 0.32% O_2 in N_2) and doped methane by DME ($\text{DME}/\text{CH}_4 = 1.8\text{--}3.2\%$) at 100 bar. Open symbols/solid lines: the neat CH_4 experiments, Crossed symbols/ dashed lines: the doped experiment by DME (1.8%), Half-open symbols/ dotted lines: the doped experiment by DME (3.2%).

Ethane experiments (Fig. 3) indicated the onset temperatures of reaction between 700 K and 825 K, depending on pressure (20—100 bar) and stoichiometry ($\Phi=0.03\text{--}47$). It was found that increasing pressure reduced the temperature required for reaction while stoichiometry had only a slight effect. Uncompleted oxidation of ethane resulted in a relatively high yield of ethylene at intermediate temperatures. Sensitivity analyses revealed the importance of reactions involving ethylperoxyl radical ($\text{CH}_3\text{CH}_2\text{OO}\cdot$) in ethane oxidation at high pressures.

The oxidation of neat DME was also studied in the flow reactor. It was found that DME conversion started at temperatures as low as 500 K. The temperature for the onset of conversion was independent of stoichiometry. Negative temperature coefficient (NTC) behaviour has been observed for all investigated stoichiometries ($\Phi=0.04\text{--}16$) whereas it was more profound for the stoichiometric mixture. The developed model compared well with the measurements under oxidizing conditions (Fig. 4), but for stoichiometric and reducing conditions the difference between the model and the experiments were considerable.

The flow-reactor measurements of ethanol oxidation revealed the onset of fuel consumption around 675 K under reducing conditions. The oxidation was postponed to 700 K for stoichiometric and oxidizing conditions. The model predictions for the major components agreed well with the measurements (Fig. 5), but it was less accurate for some intermediate

species such as C_2H_6 . Upon ignition, i.e. 725 K for the stoichiometric mixture, aldehydes were formed considerably but disappeared at higher temperatures. Using the model to reproduce ignition delay times from literature, a good agreement was found for $T > 900$ K. At lower pressures, under the conditions of both flow reactors and shock tubes, the H-abstraction reaction by HO_2 from ethanol was found to be quite important in controlling ignition.

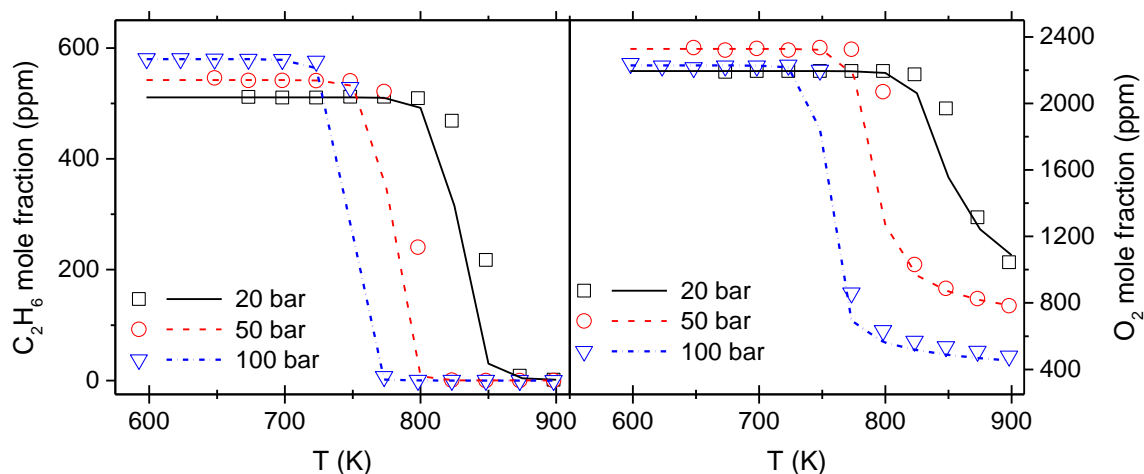


Figure 3. Results of stoichiometric ($\Phi \approx 0.85$) experiments on ethane at 20, 50, and 100 bar (511, 542, and 580 ppm of C_2H_6 , respectively). All mixtures were diluted in nitrogen. Symbols: experiments, lines: the present model.

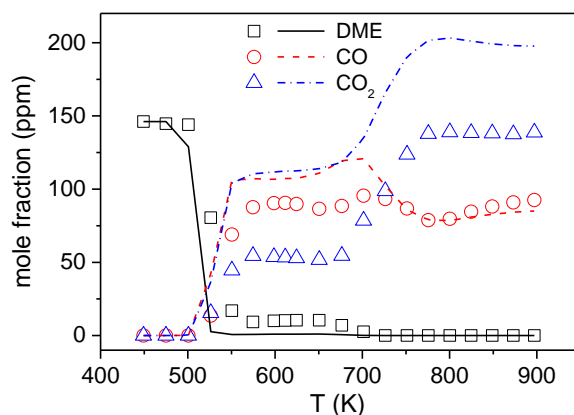


Figure 4. Results of DME oxidizing experiments at 50 bar (146 ppm of DME in N_2/O_2 , $\Phi = 0.04$).

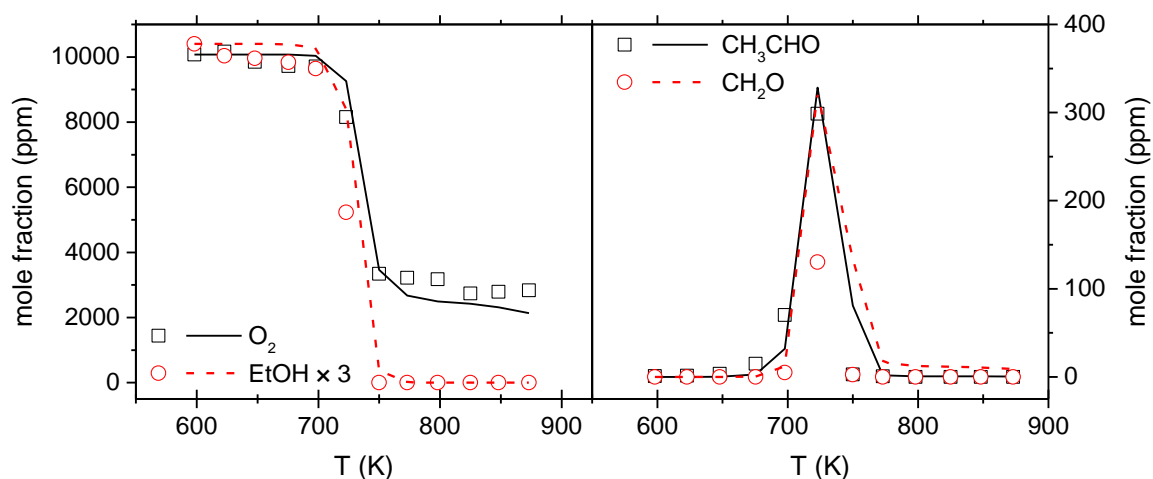


Figure 5. Results of ethanol experiments under stoichiometric conditions (0.525% ethanol and 0.0363% O_2 in N_2 , $\Phi=1.0$) at 50 bar.

3. Conclusions

The oxidation properties of hydrogen, methane, ethanol, and dimethyl ether (DME) were investigated in a laminar flow reactor at intermediate temperatures and high pressures. Results provided information about the onset temperature for reaction and the fuel consumption rate upon initiation. A detailed chemical kinetic model has been developed and validated against the measured data as well as other available combustion characteristics. It was found that while the stoichiometries of test mixtures were changed dramatically, the onset temperatures of conversion of investigated fuels were affected only slightly. Neat DME had a negative temperature dependency (NTC) at intermediate temperatures and DME addition to methane was shown to be an effective way to promote the ignition of methane. Further studies on methylperoxyl (CH_3OO) and ethylperoxyl (CH_3CH_2OO) reactions as well as the interaction between methane and DME are necessary for better understanding the oxidation of aforementioned fuels at high pressures and intermediate temperatures.

References

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